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Wetting on rough self-affine surfaces

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In this paper, we present a general investigation of the effective potential for complete wetting on self-affine rough surfaces. The roughness effect is investigated by means of the height-height correlation model in Fourier space $\sim(1+a\xi^2q^2)^{-1-H}$. The parameters H and ξ are, respectively, the roughness exponent and the substrate in-plane correlation length. It is observed that the effect of H on the free interface profile is significant for $\xi < Y$ (Y is a "healing" length), and becomes negligible for wetting-layer thickness larger than a characteristic thickness $\tau \sim \xi^u$ for long-range substrate forces. Finally, the large Y ($Y \gg \xi$) regime is characterized by a power-law scaling $\sim Y^{-2}$.

I. INTRODUCTION

The phenomenon of wetting is of fundamental physical interest and with widespread technological implications. Wetting on flat and uniform substrates is well understood, and extensive studies have been performed in this direction.[1] However, real substrate surfaces are always characterized by some degree of roughness, which depends on the method of surface treatment, the material used, and the presence of absorbed species. Recently, the role of substrate geometrical disorder (roughness) on wetting phenomena has attracted enormous attention both theoretically and experimentally.[2–7] Moreover, other types of disorder, which have been considered in wetting phenomena, include chemical impurities in the bulk,[8,9] and chemical disorder of a flat substrate.[10]

In general, the study of the asymptotic properties of thick wetting films requires a specific local and global characterization of the substrate roughness, which causes deformation of the wetting layer interface to a degree that depends on the surface tension, and the substrate interatomic potential. For fractal substrates (surface area varies as $\sim L^d$, with L the system size), the energy associated with the surface tension dominates the direct interactions with the solid and as a result complete wetting behavior occurs.[2,3] For self-affine fractals (height fluctuations vary as $\sim L^H$ with $H<1$), the effect of surface tension becomes important for "sufficiently" rough surfaces.[6] Moreover, the effect of substrate height fluctuations is similar to that of thermal fluctuations of the emerging wetting layer, and appears as a correction to the leading scaling behavior.

In previous wetting studies on self-affine rough surfaces,[6] the substrate height fluctuations were treated under the approximation in Fourier space $\sim K_s^{-1}q^{-2(1+H)}$ (K_s is related to the roughness amplitude), which neglects the low q ($\sim 1/\xi$) regime. In terms of this approach, the resulting potential (U_e) due to substrate roughness is given by $U_e \approx U + cK_s^{-1}Y^{2H}$.[6] The length scale Y (healing length) is determined by the surface tension and the interaction potential of the flat substrate problem. In this work, we shall try to investigate the roughness effect under a more precise scheme, which incorporates roughness over finite length scales more precisely. Furthermore, our calculations allow comparisons of the effect of Y and ξ, in order to determine a critical layer thickness τ, after which substrate roughness fluctuations at small length scales (characterized by H) cease to have any significant contribution on the wetting layer profile. This critical thickness can be of considerable importance in experimental adsorption studies of surface roughness since it is related with the substrate correlation length ξ.

II. THEORY FOR WETTING

In the interface approach theory,[9] the wetting phase is attracted to the substrate and forms a layer close to it. Let us denote by $h(r)$ the interface profile between the wetting layer and the nonwetting phase, by $z(r)$ the substrate profile function, and by $U[h(r)-z(r)]$ the interaction potential with the substrate [$r=(x,y)$ is the in-plane positional vector on the surface]. The regime of validity of this approach (which can describe critical or complete wetting) is confined to substrate and layer fluctuations, such that $h(r)-z(r)$ is much larger than the bulk correlation length of the wetting layer. The Hamiltonian that describes the problem is given by

$$H[h,z]=\int d^2r\{(K/2)(\nabla^b h)^2+U[h(r)-z(r)]\} \ . \qquad (1)$$

Equation (1) captures the correct scaling behavior in the limit of large wetting layer thickness. The parameter b has the value $b=1$ for interfaces governed by surface tension, and the value $b=2$ for membranes, which are governed by curvature energy. The interaction potential U results from addition of two-body substrate-adsorbate interactions, and is, in general, a nonlocal function of h and z.[5] In the following, we shall consider only the case $b=1$.

The interface profile of the wetting layer is obtained (under the constraint of no thermal fluctuations) by minimization of Eq. (1), which yields $K\nabla^2 h = U'(h-z)$. Expansion of U around a minimum value ε; $U(h-z)\approx U(\varepsilon)+(1/2)U''(\varepsilon)(h-z-\varepsilon)^2$, yields

$$K\nabla^2 h=(h-z-\varepsilon)U''(\varepsilon) \ , \qquad (2)$$

since $U'(h-z)=U''(\varepsilon)(h-z-\varepsilon)$. The Fourier trans-forms of $z(r)$ and $h(r)$ are defined by $z(r)=\int z(q)e^{i\mathbf{q}\cdot\mathbf{r}}d^2q$ and $h(r)=\int h(q)e^{i\mathbf{q}\cdot\mathbf{r}}d^2q$. After Fourier transformation of Eq. (2), we obtain for $q\neq 0$,

$$h(q)=z(q)\{U''(\varepsilon)/[Kq^2+U''(\varepsilon)]\}\ . \tag{3}$$

Fourier transformation of Eq. (1), and substitution of Eq. (3) yields

$$H[h,z]=AU(\varepsilon)+[(2\pi)^2/2]\times\int d^2q\{Kq^2U''(\varepsilon)/[Kq^2+U''(\varepsilon)]\}|z(q)|^2\ , \tag{4}$$

where the factor A denotes the average flat interface area ($A=\int d^2r$). In Eq. (4), the term $Kq^2|z(q)|^2$ represents the surface-tension cost if the free liquid interface follows the substrate fluctuations at a wave vector $\mathbf{q}$, while the term $U''(\varepsilon)|z(q)|^2$ represents the substrate interaction cost if the free interface becomes flat. In fact, the competition between substrate interaction and surface tension determines the wetting layer interface profile. The average over possible relaxations of the rough surface yields the effective potential for wetting $U_e(\varepsilon)=\langle H[h,z]\rangle$,

$$U_e(\varepsilon)=AU(\varepsilon)+[(2\pi)^2/2]\times\int d^2q\{Kq^2U''(\varepsilon)/[Kq^2+U''(\varepsilon)]\}\times\langle|z(q)|^2\rangle\ . \tag{5}$$

From Eq. (5), we observe that the knowledge of the roughness spectrum $\langle|z(q)|^2\rangle$ of the substrate surface yields all the necessary information to calculate $U_e(\varepsilon)$. In fact, the second term in Eq. (5) is the one that represents the energy cost to deform the wetting layer interface, because of substrate roughness.

III. SELF-AFFINE FRACTAL ROUGHNESS

All rough surfaces exhibit perpendicular fluctuations, which are characterized by a mean-square roughness $\sigma=\langle z(r)^2\rangle^{1/2}$ [$\langle z(r)\rangle=0$], where $\langle\ \rangle$ is an average over the whole planar reference surface. The roughness is termed "Gaussian" if $z(r')-z(r)$ is a Gaussian random variable, whose distribution depends only on the coordinates of $R=r'-r$. For an isotropic rough surface, the height-difference correlation function $g(R)$ is written as $g(R)=\langle[z(r')-z(r)]^2\rangle$, where the average is taken over all pairs of points on the surface, which are separated horizontally by the length R, as well as denotes an ensemble average over all possible roughness configurations. The height-difference correlation of any physical self-affine surface will saturate at sufficiently large horizontal lengths to the value $2\sigma^2$. It is thus characterized by a correlation length ξ,[11,12] such that

$$g(R)\sim R^{2H}\ ,\quad R\ll\xi \tag{6a}$$

$$g(R)=2\sigma^2\ ,\quad R\gg\xi\ , \tag{6b}$$

where $0<H<1$ is referred to as the "roughness" exponent, which characterizes the degree of surface irregularity.[12,13] Small values of $H\sim 0$ correspond to extremely jagged or irregular surfaces, while large values of $H\sim 1$ to surfaces with smooth hills and valleys.[12] The function $g(R)$ is related to the height-height correlation function $C(R)=\langle z(R)z(0)\rangle$ by $g(R)=2\sigma^2-2C(R)$.

The height-height correlation function $C(R)$ is related to $z(q)$ by means of a Fourier transformation; $\langle|z(q)|^2\rangle\sim\int C(r)e^{i\mathbf{q}\cdot\mathbf{r}}d^2r$.[14] In Fourier space, an analytic correlation model, which is valid in the whole range of values of the exponent $H, 0\leq H<1$, was given already in earlier roughness studies (*k-correlation model*).[14] In terms of this model, $\langle|z(q)|^2\rangle$ is given by

$$\langle|z(q)|^2\rangle=[A\sigma^2\xi^2/(2\pi)^5](1+aq^2\xi^2)^{-(1+H)}\ , \tag{7}$$

where the normalization condition $[(2\pi)^4/A]\int\langle|z(q)|^2\rangle d^2q=\sigma^2(0<q<Q_c)$ yields

$$a=(1/2H)[1-(1+aQ_c^2\xi^2)^{-H}]\quad(0<H<1)\ , \tag{8a}$$

$$a=(1/2)\ln(1+aQ_c^2\xi^2)\quad(H=0)\ , \tag{8b}$$

with $Q_c=\pi/a_0$, and a_0 the atomic spacing. The limit $H\rightarrow 0$ can be obtained from the case valid for $H>0$, if we consider the definition $(1/H)[x^H-1]\rightarrow\ln(x)$. The upper cutoff is related with the fact that any notion of fractal scaling at length scales below a_0 ceases to exist. The case of logarithmic roughness ($H=0$), as a limiting case of self-affine roughness,[14] is related to predictions of various growth models regarding the *nonequilibrium* analog[15] of the equilibrium roughening transition.[16]

IV. ANALYTIC AND NUMERICAL RESULTS FOR $U_e(\varepsilon)$

In previous calculations of the roughness effect, only the simple scaling approximation for the roughness spectrum $\langle|z(q)|^2\rangle\approx(1/K_s)(q^2)^{-(1+H)}$ was used,[6] and the final result was limited to the scaling relation,

$$U_e(\varepsilon)/A\approx U(\varepsilon)+cY^{2H}\ , \tag{9}$$

where the length scale $Y=(K/U''(\varepsilon))^{1/2}$ is the so-called "healing" length, and c is an integration constant. In fact, for length scales lower than Y the interface is flat, and substrate height fluctuations can be ignored.[6] Furthermore, Eq. (9) cannot describe the limiting case of self-affine scaling for roughness exponent $H=0$.

Logarithmic roughness ($H=0$). Calculation of the roughness effect can be achieved easily in the case of $H=0$. In this case, the substrate fluctuations reveal at sort length scales logarithmic behavior in a manner similar to those of thermal fluctuations.[14] We define the quantities $A1=-1/2Y^2(a\xi^2-Y^2)$, $B1=1/2a\xi^2(a\xi^2-Y^2)$, and the equations

$$X1=A1[(1+Q_c^2Y^2)-\ln(1+Q_c^2Y^2)]\ ;$$
$$X2=B1[(+aQ_c^2\xi^2)-\ln(1+aQ_c^2\xi^2)]\ . \tag{10a}$$

Equation (5), after substitution of Eq. (7) with $H=0$, yields the analytic expression,

$$U_e(\varepsilon)/A=U(\varepsilon)+[(K\sigma^2\xi^2)/2(2\pi)^2][X1+X2]\ . \tag{10b}$$

For $Q_c Y \gg 1$ and $Q_c \xi \gg 1$, the sum $X1+X2$ in Eq. (10b) can be simplified to the form $X1+X2 \approx [1/2(a\xi^2-Y^2)][(1/a\xi^2)\ln(aQ_c^2\xi^2)-(1/Y^2)\ln(Q_c^2Y^2)]$. If $\xi \ll Y$ or $\xi \gg Y$, the corresponding limiting expressions are given by

$$U_e(\varepsilon)/A \approx U(\varepsilon)+[(K\sigma^2)/(4\pi)^2][\ln(Q_c^2Y^2)/(aY^2)] , \quad \xi \gg Y \tag{10c}$$

$$U_e(\varepsilon)/A \approx U(\varepsilon)+[(K\sigma^2)/(4\pi)^2][\ln(Q_c^2\xi^2)/(aY^2] , \quad \xi \ll Y . \tag{10d}$$

Equation (10d) reveals a power-law behavior $\sim Y^{-2}$ of the roughness contribution as a function of Y. In fact, this analytic result will be important to determine the asymptotic behavior for large Y even for the self-affine case $H>0$. In Fig. 1, we present the case $H=0$ by the solid line.

Self-affine roughness $(0<H<1)$. In this case, we present numerical calculations of the roughness effect for various values of the roughness exponent H. The schematics depict the second term of Eq. (5) as a function of the healing length Y. The calculations have been performed with $\sigma=3$ nm, $\xi=60$ nm, and for values of the roughness exponent in the range $0\le H<1$. The particular choice for the values of σ and ξ is based on measurements of nanoscale roughness in silver films.[17]

Figure 1 shows that the roughness effect as a function of H becomes maximum for $H=0$ (logarithmic roughness). Therefore, substrate fluctuations, which resemble those of capillary waves in liquids, affect more drastically the wetting-layer profile. Furthermore, for large values of the healing length $(Y>\xi)$ all the curves appear to merge to each other, resulting in loss of any memory from the substrate fluctuation density, as described by the roughness exponent H (degree of surface irregularity). For small healing lengths Y $(Y<\xi)$, the roughness effect becomes significantly sensitive to the roughness exponent H. This is in fact the regime of validity of Eq. (9) obtained in previous studies.[6] In this case, after substitution of Eq. (7) in Eq. (5) and omission of the small wave-vector regime of the roughness spectrum, we obtain

$$U_e(\varepsilon)/A \approx U(\varepsilon)+G(H)[\sigma^2U''(\varepsilon)/(4\pi)^2a^{1+H}\xi^{2H}]Y^{2H}$$

$[G(H)=\int dx(1+x)^{-1}x^{-H}]$, with $0<x<+\infty$ for $Q_cY\gg 1$, which is indeed Eq. (9) with the constant c completely determined.

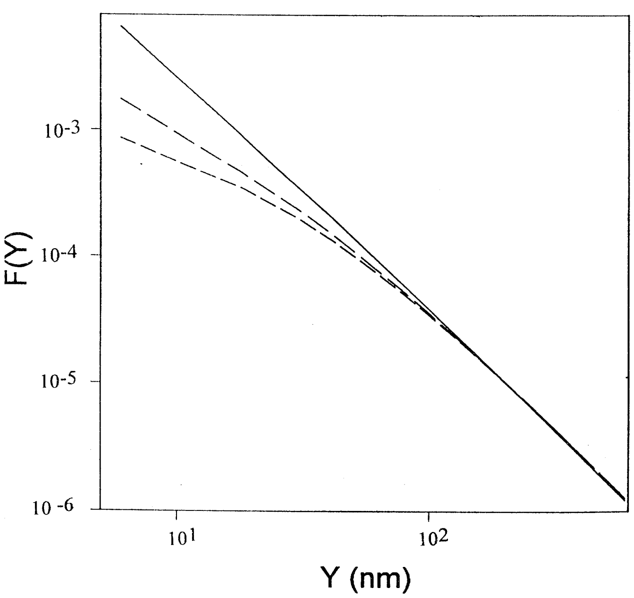

FIG. 1. Schematics for the roughness contribution in a log-log plot of $F(Y)$ versus the healing length Y. The function $F(Y)$ is given by $F(Y)=[1/(2\pi)]\int d^2q[q^2U''(\varepsilon)q^2/(Kq^2+U''(\varepsilon))][A\sigma^2\xi^2(1+aq^2\xi^2)^{-(1+H)}]$. The parameters $\sigma=3$ nm, and $\xi=60$ nm were used during the calculations. $H=0$: solid line; $H=0.5$: large dashes; and $H=0.9$: small dashes.

Critical thickness τ. Since, for $\xi\approx Y$, we obtain a crossover behavior from the regime where the free interface is controlled to a significant degree by substrate fluctuations to the regime where it is "unaffected," we estimate the effective wetting layer thickness τ, which determines such a behavior for a substrate with given in-plane correlation length ξ. If we consider long-range interactions for the flat substrate potential to the form $U(\varepsilon)\approx D\varepsilon^{1-s}+C\varepsilon^{-s}+\cdots$, we obtain $U''(\varepsilon)\approx D(s-1)s\varepsilon^{-1-s}$. Substitution in $\xi\approx Y=(K/U''(\varepsilon))^{1/2}$ yields the critical wetting-layer thickness τ,

$$\tau\approx[D(s-1)s/K]^{1/s+1}\xi^{2/s+1} . \tag{11}$$

It should be pointed out that the scaling exponent $2/s+1$ in Eq. (11) controls the crossover from the *mean-field* regime [$H<2/s+1$; asymptotic behavior dominated by the substrate potential $U(\varepsilon)$ and substrate roughness becomes irrelevant] to the *strong fluctuation* regime ($H>2/s+1$; surface tension cost dominates the original potential). For the case of van der Waals forces ($s=3$), the critical thickness scales as a function of the in-plane correlation length ξ, as $\tau\sim\xi^{1/2}$, as is predicted in previous studies.[5]

Large healing length $(Y\gg\xi)$. The effect of the substrate normal roughness σ is limited only to enhance the roughness contribution, whereas the main effect that distinguishes the various morphologies (different H) comes from the competition between ξ and Y. Furthermore, since the various curves (see Fig. 1) approach asymptotically each other for $Y\gg\xi$ and $0\le H<1$, and from Eq. (10d) the roughness contribution scales for $Y\gg\xi$ as $\sim Y^{-2}$, we can conjecture that the effective potential $U_e(\varepsilon)$ for $Y\gg\xi$ follows the scaling relation,

$$U_e(\varepsilon)\approx U(\varepsilon)+\Omega Y^{-2} \quad (0\le H<1,\xi\ll Y) , \tag{12}$$

where $\Omega\approx\{[K\sigma^2\ln(Q_c^2\xi^2)]/a(4\pi)^2\}$, with the parameter a given by Eq. (8b).

V. CONCLUSIONS

In conclusion, in our study we convoluted known information regarding wetting theories on rough surfaces with that of precise surface height-height correlation models for self-affine fractals, in order to investigate the effect of the substrate roughness on wetting phenomena. It turns out that in order for the substrate roughness to impose a significant contribution on the fluctuations of the wetting-layer profile (effect of H), the substrate correlation length ξ should be larger than the healing length Y, in agreement with previous studies.

Alternatively, it is shown that the roughness effect will contribute significantly for wetting layers of thickness smaller than a critical thickness τ, as defined by means of Eq. (11). In addition, it is shown for large healing lengths ($\xi \ll Y$) the roughness effect scales as a function of Y as $\sim Y^{-2}$ and values of H in the range $0 \leq H < 1$ [Eq. (12)].

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